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SURFACE PASSIVATION FOR III-V SEMICONDUCTOR PROCESSING: STABLE GALLIUM SULPHIDE FILMS BY MOCVD

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Abstract

Gallium sulphide (GaS) has been deposited on GaAs to form stable, insulating, passivating layers. Spectrally resolved photoluminescence and surface recombination velocity measurements indicate that the GaS itself can contribute a significant fraction of the photoluminescence in GaS/GaAs structures. Determination of surface recombination velocity by photoluminescence is therefore difficult. By using C-V analysis of metal-insulator-semiconductor structures, passivation of the GaAs with GaS films are quantified.

Introduction

Gallium arsenide and other III-V semiconductors have intrinsic properties that make them desirable for high speed electronics. Gallium arsenide in particular, has made significant inroads into the semiconductor market. Laser diodes, LEDs, metal-semiconductor field effect transistors (MESFET), high-electron mobility transistors (HEMT) and heterojunction bipolar transistors are all commercially available as GaAs devices. However, the reliability and optimum performance of GaAs devices is hindered by poor insulating layers. For example, GaAs FETs rely on a Schottky barrier to provide a modulated electric field (a MESFET device). This is clearly inferior to the metal-insulator-semiconductor structure used in silicon devices. Leakage currents are orders of magnitude lower using a metal-insulator-semiconductor devices (MISFET or MOSFET). The GaAs MESFET devices also suffer from metal-semiconductor inter-diffusion at the gate and have other reliability problems. In spite of the failings of current GaAs technology, GaAs devices are used where the limitations of silicon's intrinsic properties force the use of GaAs. If a high quality MISFET device can be made

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from GaAs, the potential uses for GaAs electronics will expand significantly.

There is a significant body of work on the passivation of GaAs.¹⁻²⁰ Recent attention has focused on the use of sulphur to terminate interface bonds of the GaAs surface (e.g. references 2, 4-7, 9, 13, 17, 19). Sulphur passivation achieves results comparable to the AlGaAs/GaAs interface, but is short lived. Significant degradation can be observed in as little as 18 hours after being exposed to ambient conditions. The sulphur passivation methods are generally solution treatments and do not lend themselves to the production requirements of micron scale devices. In this paper, recent advancements in passivating GaAs with a metastable cubic phase of gallium sulphide (GaS) are presented.

Cubic Gallium Sulphide Deposition

The chemistry of the cubic-GaS MOCVD precursor and the deposition of GaS was reported previously and will not be discussed in detail here.^{20, 21} Briefly, a cubane-core molecule [(t-Bu)GaS]₄ defines a GaS unit cell in a one-to-one (Ga-S) cubic geometry. This metastable phase of GaS is deposited in a hot walled CVD chamber by sublimation of the precursor material using argon at atmospheric pressure as a carrier gas. CVD is carried out at low temperature (350°C to 400°C) with crystallinity being maintained by the unit cell structure of the precursor. The GaS is presumed to grow epitaxially on the GaAs surface thus terminating GaAs surface states. The reactor currently used for GaS deposition is considerably inferior to those used in commercial CVD growth. The fact that a passivating interface was obtained in this system is indeed notable in itself.

Approximately 5000Å thick layers of cubic GaS were deposited on low doped (excess carriers concentration $\sim 10^{16} \text{ cm}^{-3}$) p-type and n-type GaAs wafers for photoluminescence and C-V characterization. Cubic GaS films grown on fused quartz substrates were characterized by transmission and reflection measurements in a Perkin Elmer Lambda 19 spectrophotometer. Figure 1 shows transmission plus reflection for a $\sim 5000\text{\AA}$ thick GaS film. The oscillations in the curve are due to interference fringes that were not completely compensated by adding reflection and transmission scans. The sharp absorption edge at 310nm indicates that cubic GaS is a high bandgap material of approximately 3.5 to 4eV. Further characterization of GaS films included X-ray photoelectron spectroscopy, Rutherford backscattering, TEM and X-ray diffraction and are discussed fully elsewhere.^{20, 21}

Photoluminescence Characterization

In a recent report, CVD deposited layers of cubic GaS improve the photoluminescent intensity (PLI) of both p-type and n-type GaAs.²⁰ An even more recent report shows the C-V response of a metal-GaS-GaAs capacitor exhibiting the classic high frequency response required for a MISFET device.²² Passivating GaS layers are stable under ambient conditions for at least four months. In this work we report on the nature of the PLI enhancement of cubic

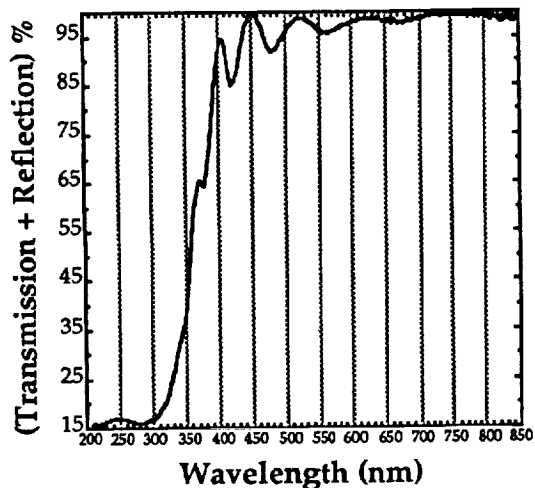


Figure 1
Transmission + reflection of cubic GaS on quartz shows a sharp absorption edge near 300nm suggesting a direct bandgap of ~4eV.

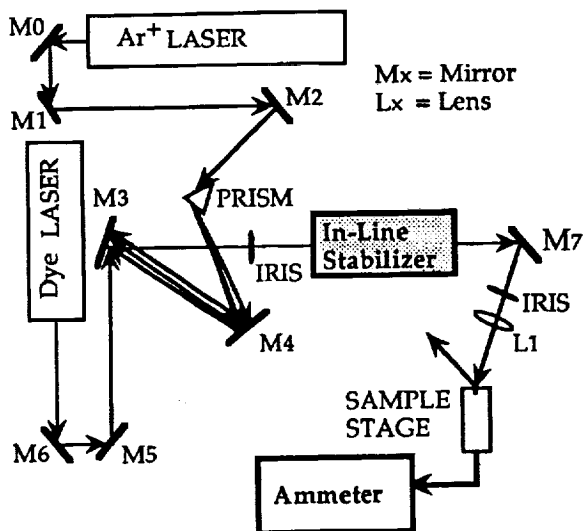


Figure 2
The optical configuration for rear PLI measurements of GaS/GaAs films. Measurements of PLI vs. absorption depth are made using various lines of an Ar+ laser and a dye laser. M3 is rotated to select argon or dye lines.

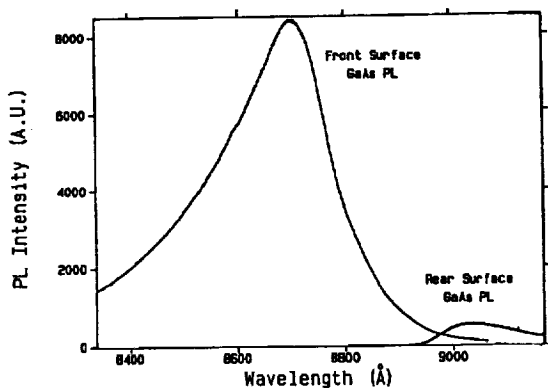


Figure 3
Room temperature GaAs PL spectra as observed from the same side as the incident laser (front) and through the GaAs (rear). Intensities are not directly comparable and are presented to show the difference in spectral content. PL intensity is in arbitrary units.

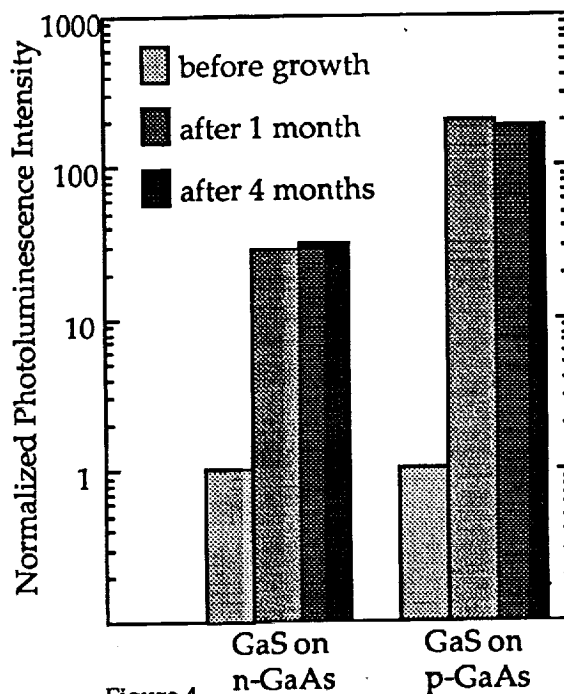


Figure 4
GaAs samples show a two order of magnitude increase in rear PL, before and after GaS deposition.

GaS layers on GaAs.

Photoluminescence intensity measurements were made by using a large area (5mm diameter) silicon photodiode placed *behind* the GaAs sample and illuminating the front of the sample with the 514nm line of an Ar⁺ laser (figure 2). This geometry has several advantages: no spectrometer or filter is necessary to remove laser light, the collection geometry is extremely repeatable and measurements can be made quickly with no additional sample preparation. Inherent in this PL system is that only the spectral tail of the PL is detected (figure 3). This generally does not present a problem because of the good match between the detector's spectral response and the radiation emitted by the GaAs. Data comparing the PLI before and after cubic GaS deposition on GaAs is shown in figure 4. Both p-type and n-type samples show two orders of magnitude increase in PLI after GaS deposition.

The relationship between PLI and the parameters of surface recombination velocity (S_v), surface depletion width (w) and absorption depth of the incident laser radiation ($1/\alpha_v$) for a semi infinite slab is given in equation 1.^{23,24}

$$PLI = Nk \exp\{-\alpha_v w\} \exp(-\alpha_{pl} d) \frac{\alpha_v L_p}{(\alpha_v L_p)^2 - 1} \cdot \left[\frac{S_v/D_p + \alpha_v}{S_v/D_p + 1/L_p} - \frac{1}{\alpha_v L_p} \right] \quad (1)$$

Where: N is the number of photons/sec of the incident light entering the semiconductor; w is the width of the space charge at the front surface; d is the thickness of the sample which a photon from recombination must travel to reach the detector; L_p is the diffusion length of minority carriers; S_v is the surface recombination velocity at the edge of the front surface depletion region; k is a system constant which includes the optical efficiency of the collection; system and the radiative efficiency of the recombination of minority carriers; α_{pl} is the absorption coefficient of the photoluminescent radiation; α_v is the absorption coefficient of the laser radiation.

An increase in PLI can be interpreted as an increase in radiative recombination in the bulk due to a decrease in surface depletion width or surface recombination velocity.

Using equation 1 the depletion width and surface recombination velocity are obtained by fitting PLI vs. $1/\alpha_v$, where α_v is the absorption coefficient in GaAs of the laser radiation and $1/\alpha_v$ is the absorption depth. Using the approximations: $S_v/D_p \gg 1/L$, $L \gg 1/\alpha_v$, $1/\alpha_{pl} \gg 1/\alpha_v$, and in the absence of a depletion region equation 1 reduces to:

$$PLI = \frac{NK}{L_p} \cdot \left[\frac{1}{\alpha_v} + \frac{D_p}{S_v} \right] \quad (2)$$

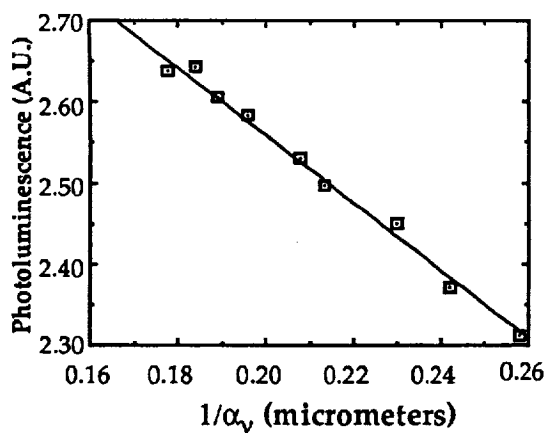


Figure 5
GaS/GaAs exhibits increasing PL with decreasing absorption depth.

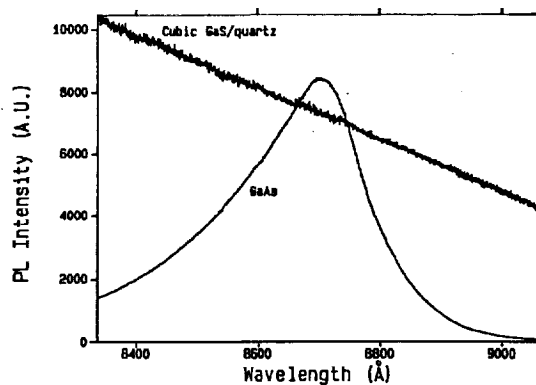


Figure 6
Front PL spectra of bare GaAs and GaS on quartz. Intensities are not directly comparable and are presented to show the difference in spectral content. PL intensity is in arbitrary units.

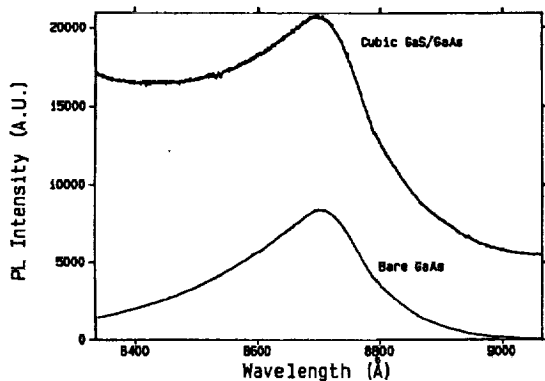


Figure 7
Front PL spectra of bare GaAs and GaS on GaAs. Intensities are both to the same scale, in arbitrary units.

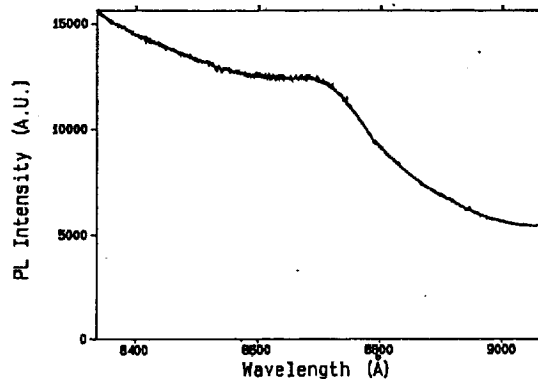


Figure 8
The difference between the PL of GaS/GaAs and bare GaAs from figure 7 suggests components of both GaS and GaAs spectra.

The intercept of PLI vs. $1/\alpha_v$ yields $-D_p/S_v$. To further characterize the GaS/GaAs interface, surface recombination velocity measurements were made. Absorption depth was varied using a tunable dye laser in the 575nm to 630nm range. For any sample PLI vs. $1/\alpha_v$ must have a positive slope. The physical argument is simple; electron hole pairs are generated further from the surface with increasing absorption depth and thus have a lower probability of diffusing to the surface and recombining nonradiatively. Hence more carriers recombine radiatively in the bulk. In the limit where S_v approaches zero, D_p/S_v approaches infinity and PLI vs. $1/\alpha_v$ has zero slope. Surprisingly, the cubic GaS/GaAs interface exhibits the exact opposite characteristic having a *negative* slope (Figure 5). It was initially assumed that the deposition of the GaS had somehow affected the bulk material by altering the doping profile, stoichiometry or other bulk parameter. However after removing only the GaS layer by etching, PLI vs. $1/\alpha_v$ returned to the characteristic positive slope. One must conclude that aberrant PLI vs. $1/\alpha_v$ data is due to the nature of the GaS/GaAs interface or the GaS itself.

To separate the effect of the GaS from the GaAs, PL of GaS grown on SiO₂ was compared to the GaAs PL spectrum. Spectrally resolved measurements were made using 1.25 meter grating spectrometer and a cooled silicon CCD array. The 514nm line of an Ar⁺ laser was used for excitation. A comparison of spectral content of GaAs and GaS photoluminescence is shown in figure 6. The GaS shows emission in the wavelength range of the GaAs PL spectrum. The emission of PL from GaS is somewhat surprising considering that absorption in the visible is less than 10% and it appears to have bandgap in the 3eV to 4eV range. The GaS PL emission does offer an explanation for the S_v data; as the absorption depth of the laser excitation decreases in the GaAs it is also decreasing in the GaS. Greater absorption in the GaS in turn increases the GaS PL emission. The S_v data can now be interpreted in one of two ways. If the GaS/GaAs interface is nearly ideal and the PLI vs. $1/\alpha_v$ line has zero slope, the GaS PL component will tend to push the slope in the negative direction. On the other hand, GaS may be the dominate PL component, masking any PL signal the GaAs contributes. In this case PLI data is not a valid indicator of the GaS/GaAs interface quality.

Figure 7 shows the *front* PL spectra of GaS/p-GaAs and GaAs with a bare surface. The most striking feature of the spectra is that the PL as seen from the rear (i.e. below 9000Å) has greatly increased compared to the bare GaAs. The *rear* PL is clearly dominated by the GaS. Subtracting the GaAs spectrum from the GaS/p-GaAs yields the net PL of the additional GaS layer shown in figure 8. By comparing figure 6 with figure 8 the spectral content of the GaS cap appears to be a weighted sum of the GaS and GaAs spectra. Although there is a significant GaS component there is also an increase in GaAs emission, indicating that there is some measure of passivation provided by the GaS film.

Assuming that the GaS contributes significantly to the PL, one would assume that thicker GaS layers would yield larger PL signals. This was not observed. To determine the component of GaS PL in the PL spectrum of GaS/GaAs, spectrally resolved front PL of different thickness layers of GaS on GaAs were compared. The CVD process does not yield a uniform layer of GaS on

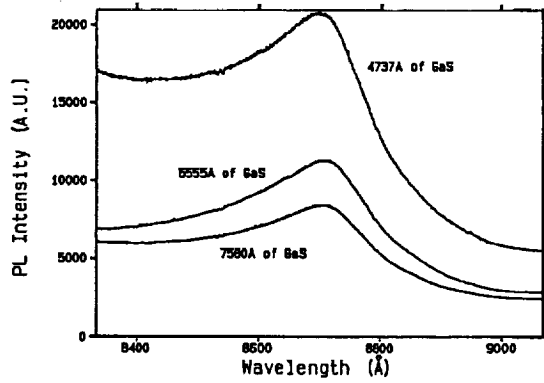


Figure 9
Front PL spectra of GaS/GaAs with three different thicknesses of GaS. Intensities are all to the same scale, in arbitrary units.

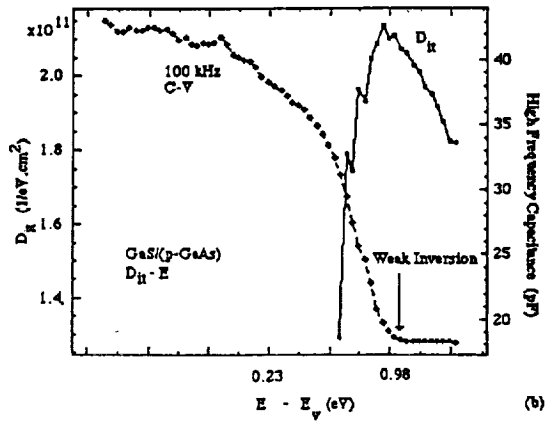
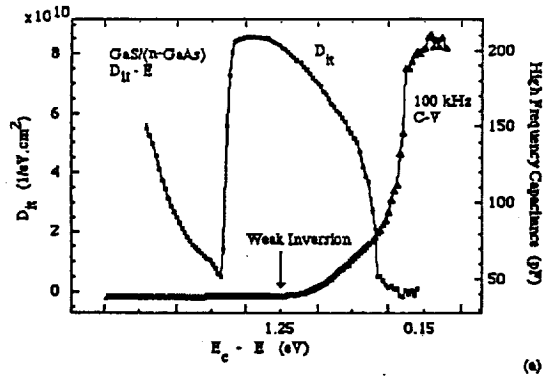


Figure 10
Interface trap density as a function of energy inside the bandgap at the interface of a) GaS/n-GaAs and b) GaS/p-GaAs.

the GaAs, therefore it is possible to examine different GaS thicknesses on the same GaAs substrate. This minimizes the possibility that the GaS/GaAs interface quality is changing when comparing different GaS thicknesses. Figure 9 shows the PL from three different thicknesses of GaS on the same piece of p-GaAs. A clear trend of higher PL with decreasing GaS thickness is shown. This evidence runs counter to the argument that the PL is dominated by GaS. Increasing PL with decreasing GaS thickness may be related to deposition artifacts but clearly the issue needs further study. Although front and rear PL indicate an improved GaAs interface, verification of the interface quality by some other means is obviously required.

C-V Characterization

High frequency C-V data and density of surface states for n-type and p-type GaAs with GaS layers are shown in figure 9. Both the n-type and p-type GaAs samples show surface state densities in the $10^{11}/\text{eV}\cdot\text{cm}^2$ range indicating that GaAs has been passivated to some degree. In the case on n-type GaAs, distinct accumulation and inversion regions in the C-V curve are present which is characteristic of a high quality interface. The n-type GaAs C-V data are a remarkable result. It clearly shows that the interface is of sufficient quality to fabricate an FET device. Full details of the C-V measurements will be published in an upcoming paper.

Conclusion

Passivation of GaAs with cubic GaS has been observed using photoluminescence and C-V analysis. Spectrally resolved PL can separate out the PL bias of GaS films and is the preferred indicator of passivation over an integrated PL intensity signal. An accounting of the GaS PL, its origin and its full effect on GaS/GaAs spectra are not yet complete and more work in this area is needed. The C-V data are evidence that PL data are *qualitatively* valid, but using PL as a quantifying parameter will take considerably more effort in understanding of GaS and the GaS/GaAs interface.

References

1. R. J. Nelson, J. S. Williams, H. J. Leamy, B. Miller, H. C. Casey, Jr., B. A. Parkinson, and A. Heller, Appl. Phys. Lett. 36, 76 (1980).
2. J. Massies, J. Chaplart, M. Laviron, and N. T. Linh, Appl. Phys. Lett. 38, 693 (1981).
3. S. D. Offsey, J. M. Woodall, A. C. Woodall, A. C. Warren, P. D. Kirchner, T. I. Chappell, and G. D. Pettit, Appl. Phys. Lett. 48, 475 (1986).
4. C. J. Sandroff, R. N. Nottenburg, J. C. Bischoff, and R. Bhat, Appl. Phys. Lett. 51,

- 33 (1987).
5. R. S. Besser and C. R. Helms, Appl. Phys. Lett. 52, 1707 (1988).
 6. M. S. Carpenter, M. R. Melloch, M. S. Lundstrom, and S. P. Tobin, Appl. Phys. Lett. 52, 2157 (1988).
 7. D. Liu, T. Zhang, R. A. LaRue, J. S. Harris, Jr., and T. W. Sigmon, Appl. Phys. Lett. 53, 1059 (1988).
 8. M. Tabib-Azar, A.S. Dewa and W.H. Ko, Appl. Phys. Lett., pp. 206-208 (1988).
 9. K. M. Geib, J. Shin, and C. W. Wilmsen, J. Vac. Sci. Technol. B 8, 838 (1990).
 10. S. Shikata, H. Okada, and H. Hayashi, J. Appl. Phys. 69, 2717 (1991).
 11. S. R. Lunt, P. G. Santangelo, and N. S. Lewis, J. Vac. Sci. Technol. B 9, 2333 (1991).
 12. S. A. Chambers and V. S. Sundaram, J. Vac. Sci. Technol. B 8, 2256 (1991).
 13. Y. Wang, Y. Darici, and P. H. Holloway, J. Appl. Phys. 71, 2746 (1992).
 14. N. Barbouth, Y. Berthier, J. Oudar, J.M. Moison, and B. Bensoussan, J. Electrochem. Soc. 133, 1663 (1986).
 15. H.H. Lee, R. J. Racicot, and S. H. Lee, Appl. Phys. Lett. 54, 724 (1989).
 16. K. Ueno, H. Abe, K. Saiki, A. Koma, H. Oigawa, and Y. Nannichi, Surf. Sci. 267, 43 (1992).
 17. B. A. Cowans, Z. Dardas, W. N. Delgass, M. S. Carpenter, and M. R. Melloch, Appl. Phys. Lett. 54, 365 (1989).
 18. C. J. Spindt, D. Liu, K. Miyano, P. L. Meissner, T. T. Chiang, T. Kendelewicz, I. Lindau, and W. E. Spicer, Appl. Phys. Lett. 55, 861 (1989).
 19. T. Tiedje, K. M. Colbow, D. Rodgers, Z. Fu, and W. Eberhardt, J. Vac. Sci. Technol. B 7, 837 (1989).
 20. A. N. MacInnes, M.B. Power, A.R. Barron, P. Jenkins, A.F. Hepp, Applied Physics Letters, Vol. 62, No. 7, pp. 771-713 (1993).
 21. A. N. MacInnes, M.B. Power, A.R. Barron, Chem. Mat. Vol. 4 p.11-13 (1992).
 22. M. Tabib-Azar, S.Kang, A.N. MacInnes, M.B. Power, P. Jenkins, A.R. Barron and A.F. Hepp to be published.
 23. K. Mettler, Applied Physics, No.12, p.p. 75-82, (1977).
 24. R.R. Chang, R. Iyer, D.L. Lile, Journal of Applied Physics, Vol. 61 (5) pp. 1995-2004, (1987).

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